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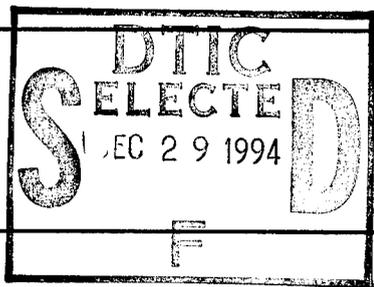
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The adsorption and dissociation of trimethylgallium (TMG, $Ga(CH_3)_3$) on the Si(001) surface has been studied using Scanning Tunneling Microscopy (STM). The products of TMG dissociation are identified by their bonding location with respect to the underlying Si(001) lattice, by bias dependent imaging and from detailed counting statistics. TMG is found to adsorb dissociatively at room temperature, yielding a methyl group and a dimethylgallium fragment bound to the surface. The $Ga(CH_3)_2$ groups produced by TMG dissocation are somewhat mobile at room temperature but are bonded more strongly near surface defects. Further dissociation yields gallium atoms on the surface, but no additional methyl groups. It is proposed that this second stage of reaction involves an intramolecular reaction to produce ethane, which desorbs into the gas phase, and gallium atoms. The gallium atoms are observed to arrange into single rows of gallium dimers which bind epitaxially on the Si surface. Heating the surface to 150 °C completely decomposes the DMG fragments, yielding Ga atoms and CH_3 groups.

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Introduction

Epitaxial growth of III-V semiconductors on silicon is important because of the possibility of using integrated silicon/III-V devices in a variety of applications, such as optoelectronics. III-V compound epitaxy, whether on silicon or III-V substrates, is usually done by metalorganic molecular beam epitaxy (MOMBE) or metalorganic chemical vapor deposition (MOCVD), using as precursors simple organometallic compounds which contain the III-V semiconductor's constituent atoms. For example, GaAs is typically grown by MOCVD using trimethylgallium (TMG, $Ga(CH_3)_3$) as a gallium source and arsine (AsH_3) or trimethylarsine as an arsenic atom source. An understanding of the adsorption and decomposition of organometallic molecules such as TMG on surfaces is thus relevant to controlling the chemistry in these important semiconductor-device production processes.

The adsorption and decomposition of TMG on silicon surfaces has been studied by a number of groups [1-7]. R. I. Masel and coworkers [3, 5-7] investigated the decomposition of TMG on Si(001) at a variety of coverages and temperatures. Based on their X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), temperature-programmed desorption (TPD), and electron energy-loss spectroscopy (EELS) results, they suggested a decomposition mechanism in which an adsorbed TMG molecule undergoes sequential loss of two methyl groups as methane molecules (which escape into the gas phase), resulting in one gallium atom and one carbon atom deposited on the surface. They concluded that carbon incorporation was an integral part of TMG decomposition on Si(001). Flores et al. [1] used static secondary-ion mass spectroscopy (SSIMS), TPD, and Auger electron spectroscopy (AES) to study TMG decomposition on Si(001). Their SSIMS results suggested that Ga-C bonds cleave and CH_3 groups bind directly to the silicon substrate even at temperatures as low as 115 K, and that the loss of methyl groups by TMG molecules to the surface goes to completion by 420 K (150 °C). Thus, there is some disagreement in the literature over the mechanism by which TMG decomposes, and the ultimate fate of the carbon atoms on the surface. This is an important issue, as incorporated carbon is one of the chief impurities often found in GaAs films grown by MOCVD or MOMBE and controls the doping in many applications [8].

To further elucidate the mechanism of adsorption and decomposition of TMG on Si(001), we have studied this adsorption and decomposition with atomic resolution using scanning tunneling

microscopy (STM). We identify the TMG fragments on surfaces heated to a variety of temperatures based on adsorption site symmetry, bias-dependent imaging, and detailed counting statistics. Based on these results, we propose a mechanism in which TMG adsorbs dissociatively to yield a methyl group and a dimethylgallium (DMG) fragment bound to the surface. The DMG fragments can further decompose, losing two methyl groups simultaneously as a (gas phase) ethane molecule, to leave gallium atoms bound to the surface. The result of decomposition of a TMG molecule is thus one gallium atom and one carbon atom bound to the Si(001) substrate.

Experimental

Our experimental apparatus has been described in detail previously [9, 10]. All experiments are carried out in a room-temperature, ion pumped stainless steel UHV chamber (base pressure < 10^{-10} Torr). Our STM consists of a chemically etched tungsten tip mounted on a piezoelectric tube scanner (Stavely Sensors, Inc.) which is attached to the end of an Inchworm motor (Burleigh Instruments) for coarse approach. In tunneling experiments, voltages are applied to the sample in an electrically isolated tunneling stage. Samples can be resistively heated on a separate heating stage by passing current directly through the sample. Trimethylgallium and other dosing gases can be introduced into the chamber through a precision leak valve.

Samples of n-type Si(001) wafers (oriented to within 0.1 degree; Wacker-Chemitronic GmbH) were rinsed with methanol and then exposed to ozone produced by a quartz mercury-vapor lamp (UVP Inc.) to further minimize carbon contamination. After introducing the sample into ultrahigh vacuum (UHV) through a load-lock, samples were degassed for 1-2 hours at 630 °C and then annealed to 1100 °C to remove the oxide and produce a clean, well-ordered Si(001)-(2x1) suface. After cooling, the sample was moved to the STM and imaged to verify a well ordered surface, free from contamination and with a low defect density. The tip was then withdrawn and the sample was exposed to a selected pressure for a selected time interval, typically $5x10^{-9}$ Torr for 40 s., of trimethylgallium (vapor pressure 226 Torr at 300 K; Strem Chemicals). The tip was brought back into tunneling and the dosed surface was imaged. Some experiments were performed in which the TMG was introduced while the tip was in tunneling range in

order to identify the role of defects and other surface inhomogeneities on the decomposition process.

Images are recorded with a tunneling current of 0.3 - 0.5 nA and voltage magnitude of 1.5 - 3.0 V. Images can be acquired with either negative or positive sample bias polarity, giving images of filled or unfilled surface electronic states, respectively. Large-scale STM images showed that the average terrace width on the surfaces of these samples was 1000 - 1500 Å.

Results and Discussion

I. TMG Fragments

Figure 1 shows a large scale STM image of a Si(001) surface dosed at 300 K with 5×10^{-9} Torr of TMG for 40 seconds. This surface exhibits a large number of features which are not present on clean silicon and which we attribute to TMG or TMG fragments. STM images of Si(001) exposed to TMG show three types of surface species. The most prominent features are large white protrusions (height 3-4 Å), labeled "DMG" in figure 1, which appear scattered randomly upon the surface. The second main surface features are small islands, approximately one dimer row wide, running perpendicular to the dimer rows of the Si(001) substrate. Several such features are labeled "Ga" in figure 1. These two features will be identified as dimethylgallium fragments and rows of gallium atoms, respectively, as discussed below. The third type of surface fragment is difficult to see in figure 1 but is more easily observed in the smaller area, higher-resolution STM image shown in figure 2. This third feature consists of a small, low protrusion sitting atop an Si dimer, displaced to one side of the dimer. These features, labeled "CH3" in figure 2, will be identified as CH_3 groups.

As shown in fig. 3, heating the substrate to 150 °C for two minutes prior to imaging results in the nearly complete disappearance of the features labelled "DMG"; instead, the only two structures observed are the "CH3" features and the "Ga" islands. At all temperatures between 300 and 450 Kelvin, all observed molecular fragments can be identified as one of the three fragments labeled "Ga", "CH3", or "DMG". Furthermore, careful examination of the "Ga" features reveals that each "Ga" island is composed of an integral number of subunits. These can be seen more clearly in figure 4, a filled-electronic-state STM image of several of the "Ga" island features. Inspection of figure 4 shows that while the "Ga"

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islands vary in length, each island consists of an integral number of "building blocks" which are labelled "Ga2" in figure 4. This will be discussed further below.

Further information regarding the symmetry and electronic properties of the nascent products of adsorption is obtained by comparing images of a single region acquired at negative and positive sample bias, probing occupied and unoccupied electronic states, respectively. Figure 5 shows such images at negative (5a, -2.4 V) and positive (5b, +2.7 V) of a single region containing the products of TMG dissociation. A comparison of figures 5a and 5b shows that while at negative sample bias each "Ga2" feature appears as two lobes of intensity, at positive sample bias each "Ga2" feature appears as a single large protrusion. Conversely, the DMG fragments appear as a single high protrusion at negative bias, but at positive bias each DMG fragment appears as two lobes. The fragments identified as CH_3 do not change significantly between filled-state and empty-state images. Note that the underlying lattice also changes in appearance between negative and positive bias. In particular, while at negative bias the Si=Si dimers show a maximum directly above the Si-Si bond, at positive bias the silicon dimers exhibit a deep minimum in apparent height at this same location. This difference is well understood to arise from the differing symmetries of the occupied π and unoccupied π^* orbitals of the dimer [11]. Although the features in fig. 5a and 5b show some slight asymmetries which can be attributed to a slightly asymmetric STM tip, the appearance of these features as a function of bias has been reproduced on other samples and using different tips. Figure 6 schematically depicts the appearance and symmetry with respect to the underlying Si(001) lattice for all three types of molecular fragments observed. We also find that the apparent height of the various features changes substantially as a function of bias polarity. Table I lists the apparent heights of the three types of features when imaging both filled and unfilled electronic states.

A) Structure and Bonding of Gallium Dimers on Si(001)

We consider first the structure and bonding of gallium on the surface. Figure 4 shows a filled-electronic-state STM image (acquired at negative sample bias) of several of the "Ga" island features, from a sample which has been heated to 450 K. Careful examination of figure 4 as well as the images obtained without heating (figures 1 and 2) demonstrates that while the "Ga" islands vary in length, each

island consists of an integral number of "building blocks" which are labelled "Ga2" in figure 4.

Identification of these features is straightforward in light of previous STM studies on the Ga/Si(001) system and similar systems. Island features similar in appearance to the "Ga" islands are often observed on Si(001) surfaces dosed with elemental gallium [12-14] and other group III metals [15-19], and such features are identified as rows of metal-atom dimers on the Si surface. Theoretical calculations by a number of groups [20-22] support the dimer-row model as the preferred configuration for group III metal atoms on Si(001). We thus identify the long row features as rows of gallium, composed of gallium dimers, which appear as "Ga2" features as shown above.

The appearance of the dimers in both the negative- and positive-bias images can be understood by considering the nature of the chemical bonds in the dimer and the mechanism of STM imaging. At negative bias the STM images filled electronic states (molecular orbitals), in this case the Ga-Si bonds [20]: because silicon is more electronegative than gallium, Si atoms draws electron density away from Ga atoms, giving the Si-Ga back-bonds a higher, more localized electron density than the Ga-Ga sigma-bond. Similarly, the most prominent unfilled states, imaged at positive sample bias, are most likely the two "unused" Ga(N=4) sp^3 atomic orbitals of the (trivalent) gallium atoms, which are located almost directly above the Ga atoms. Recent calculations by Yamazaki et al. [22] gave just this result and interpretation for STM images of the isoelectronic Al:Si(001) system.

There has been some controversy in the literature over the orientation of the Ga dimers with respect to the underlying Si lattice. Two geometries have been proposed: a parallel ad-dimer geometry [21] shown in figure 7a, and a perpendicular geometry [12-14, 23] shown in figure 7b. Recent first-principles total-energy calculations by Northrup et al. [21] yielded the parallel ad-dimer structure as the lowest energy structure. The positive-bias image in figure 5b shows the Ga dimers on both terraces as ovals with their long axes oriented parallel to the underlying silicon dimers, suggesting that they are bonded parallel to the silicon dimers as shown in figure 7a, in agreement with the theoretical prediction. This is in contrast to the structure suggested by Nogami et al. [12-14] and by Bourguignon et al. [23]. Irrespective of which structural model is correct, the important fact is that each Ga2 feature consists of two gallium atoms bonded together in a dimer.

B) Structure and Bonding of Methyl Groups on Si(001)

Next we turn to the small white protrusions labeled "CH$_3$" in figures 2 and 3. Consideration of the symmetry of these features with respect to the Si(001) lattice can help us to identify these fragments. Figure 8 shows a high-resolution image of several of these fragments, with horizontal grid lines marking the tops of the dimers rows of the Si(001) dimer lattice. As schematically depicted in figure 6, each "CH$_3$" feature consists of a small protrusion sitting exactly on top of the position of one silicon atom of a dimer: on top of the dimer, displaced to one side. This is just the bonding symmetry one would expect of a methyl group, as shown in figure 9. A CH$_3$ group needs only one bond to the Si surface in order for the central carbon atom to achieve 4-fold coordination. This bond can be formed by breaking the weak Si-Si π-bond between two Si atoms of a dimer, and bonding the methyl group to one of the atoms. The feature labeled "CH$_3$" thus has the symmetry with respect to the silicon lattice that one would expect for a methyl group. This is also the same symmetry which was previously observed for SiH$_3$ groups (which are isoelectronic with CH$_3$ groups) adsorbed on Si(001) [24]. Our identification of the CH$_3$ features as adsorbed methyl groups is confirmed in separate experiments in which we dosed the Si(001) surface with methyl chloride (CH$_3$Cl) and imaged the resultant products at room temperature and after thermal annealing [25]. In those experiments, we observed two distinct types of new features on the surface. One of these had the same appearance as the surface-bound chlorine atoms previously studied in STM by Boland [26], while the second type of fragment has exactly the same appearance as the CH$_3$ features produced by the interaction of TMG with Si(001). Thus, the use of methyl chloride as a "calibration" molecule confirms our identification of the "CH$_3$" features as adsorbed methyl groups. .

Our observation of partial dissociation of TMG to produce methyl groups at 300 Kelvin is also supported by previous studies using a number of experimental techniques. In SSIMS studies of TMG-dosed Si(001) surfaces, Flores et al. [1] observed SiCH$_3^+$ ions at sample temperatures as low as 115 K, confirming that methyl groups do break off of the TMG molecules and stick to the silicon substrate even at low temperatures. In High Resolution EELS (HREELS), TPD and AES studies of the adsorption and decomposition of methyl iodide on Si(001), Colaianni et al. [27] found that methyl groups on Si(001) were stable at temperatures up to 600 K.

While our experiments confirm that the features labelled "CH$_3$" are directly associated with the presence of a methyl group, the exact

bonding configuration is not certain because STM is primarily sensitive to the local electronic structure. CH_3 fragments, like the isoelectronic SiH_3 fragment and H atoms, bond to a Si=Si dimer by breaking the weak π-bond of the Si=Si dimer in order to form a much stronger Si-C (or Si-Si or Si-H) sigma-bond. In all three cases, this leaves the other dimer of the Si=Si dimer as a formal radical, or "dangling bond". In all three cases, while the fragments are spatially closer to the tip, the "dangling bonds" posess electronic states near the Fermi level which could permit facile electron tunneling both into and out of the surface. Thus, the protrusions observed in the STM images might correspond to the location of the CH_3 molecular fragment (i.e., geometric contrast), or might correspond to the location of the "dangling bond" (electronic contrast). Indeed, bias-dependent STM images of SiH_3, CH_3 and H appear significantly different, even though these three species all have nominally the same binding configuration, suggesting that the simple "dangling bond" picture of the electronic structure is incomplete. Note, however, that either interpretation of the protrusions allows us to conclude that each "CH_3" site corresponds to exactly one methyl group.

C) Dimethylgallium Fragments

Finally, we consider the large protrusions labeled "DMG" in figure 1. We find that the surface coverage of these features is directly proportional to the total exposure (pressure x time) of TMG, for exposures less than one Langmuir. Furthermore, in experiments where we dose with TMG while in tunneling (see below), we observe that these features begin to appear on the surface as soon as the TMG is turned on, but no further increase is observed when the TMG is shut off. We conclude that these features are either molecular TMG, or a fragment of TMG that forms immediately upon adsorption. As discussed above, previous work has shown that C-Ga bonds are the first bonds of TMG to break on Si(001), that this bond cleavage occurs even below room temperature [1], and that the CH_3 groups do not decompose further at the temperatures used in the current study (below 600 K) [27]. We therefore conclude that the "DMG" features must be some fragment of the form $Ga(CH_3)_n$, n = 0 - 3. Figure 10a shows a high-resolution STM image of several of these features. As shown by the gridlines in this figure, the "DMG" features have the local symmetry shown in figure 6, with each fragment positioned on top of a dimer row, displaced to one side, and sitting symmetrically

between the positions of two silicon dimers in the underlying dimer row. This symmetry is observed consistently for these features.

We can gain some information about these features from bias-dependent imaging. As described above, figure 5 shows STM images of the same area at negative and positive bias (filled and empty states). Several "DMG" features are identified in the filled-state image, and the same features are shown in the empty-state image. Close examination of figure 5b shows that each "DMG" shows a double-lobed structure at positive bias: each feature consists of two lobes of intensity. "DMG" groups on alternate terraces separated by a monatomic step in this image have their lobes oriented in perpendicular directions, indicating that this shape is real and not the result of a double tip or other artifact. This double-lobed shape suggests that each "DMG" has two equivalent moieties extending up away from the surface, which suggests that the "DMG" features are in fact dimethylgallium groups. The "DMG" features can be identified conclusively as dimethylgallium fragments by considering the counting statistics, the relative numbers, of the various species appearing on the Si surface, as discussed in the following section.

II. Decomposition Mechanism

The mechanism of TMG adsorption and decomposition on the Si(001) surface can be studied using experiments in which the surface is dosed with TMG while tunneling, permitting the same area of the surface to be imaged before and after its interaction with TMG. Figure 11a shows an area of the clean surface just before dosing, and figures 11b and 11c show the same area after progressively longer exposure times (higher TMG coverages). The images in figures 11b and 11c were recorded after 4 minutes and 10 minutes of TMG exposure, respectively. We see that, on this time scale, both "DMG" features and gallium dimers appear on the surface (the resolution in these images is not good enough to observe methyl groups, which are much less prominent features). If we continue to observe such a surface, we find that the surface concentrations of both "DMG" and Ga2 remain constant after dosing is completed, up to 10 hours after dosing.

The ratio of DMG features to Ga2 features varies between 0.5 and 4.0 for different silicon samples, but does not change with time on a given sample. However, as shown in fig. 12, heating the sample to 150 °C strongly decreases the number of DMG fragments and increases the number of Ga2 features. The upper image (fig. 12a),

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depicts the surface before heating, with a DMG:Ga2 ratio of approximately 1:1. Fig. 12b shows the same sample (albeit a different region) after heating to 150 °C, with a DMG:Ga2 ratio less than 0.05:1. As mentioned above, high-resolution images of heated surfaces show that the methyl groups also remain after heating. On dosed samples imaged before and after heating, we find that the Ga2 surface concentration increases after heating by just one half the pre-heating surface concentration of the "DMG" groups. From this observation, we conclude that the "DMG" species is a TMG fragment containing exactly one gallium atom. This fragment decomposes further upon heating to 150 °C: the gallium atom is released onto the surface to combine with another Ga atom to form a Ga2 dimer.

The counting statistics of CH_3 groups on the surface can provide additional insight into the reaction mechanism. Surprisingly, our counting statistics indicate that while heating a TMG-exposed sample clearly increases the number density of elemental gallium atoms on the surface, the density of methyl groups remains *constant*. Thus, while the ratios N_{CH3}/N_{DMG} and N_{CH3}/N_{Ga2} vary from sample to sample and are changed upon heating, these changes are correlated such that the ratio of methyl groups to gallium atoms (in all forms) is constant. We find that this ratio is always unity, i.e.,

$$\frac{N_{CH3}}{N_{DMG} + \dfrac{N_{Ga2}}{2}} = 1.0 \pm 0.1 \qquad (1)$$

These counting statistics have several important implications. First, they imply that the decomposition of TMG, whether occurring spontaneously or thermally induced, occurs in such a way that for every gallium atom that sticks on the surface, one methyl group is ultimately deposited on the surface. Thus, two of the three methyl groups in each TMG molecule must be removed from the surface region and, presumeably, desorb into the gas phase in some chemical form. The statistics also indicate that for each DMG fragment observed, one methyl group has already moved to the substrate; this indicates that the fragments labelled "DMG" must be dimethyl gallium or monomethyl gallium. Since heating increases the number of Ga atoms on the surface but not the number of methyl groups, we may conclude that any CH_3 groups remaining on the DMG fragments must leave the surface during the thermal decomposition. This could conceivably occur for dissociation of monomethyl fragments, which could release methyl radicals or ions into the gas phase. However, the most reasonable proposal is that the DMG fragments are

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dimethylgallium fragments, and that dissociation of these fragments involves an intramolecular reaction of the two CH_3 groups to produce a molecule of ethane (which leaves into the gas phase) and an atom of gallium. Our experiments indicate that the decompositon of the DMG species occurs in a single step, with no intermediates observed. The number densities of molecules in our experiments are very low, so that intermolecular reactions of the DMG fragments with other surface species are negligible. This might not be true, however, at higher coverages.

Based on our observations and a statistical analysis of the STM data, then, we assign the "DMG" fragments as $Ga(CH_3)_2$ (dimethylgallium), and deduce the following mechanism for the adsorption and decomposition of trimethylgallium on Si(001) at low coverage:

$$Ga(CH_3)_3 \text{ (g)} \quad \text{-->} \quad CH_3 \text{ (ads)} + Ga(CH_3)_2 \text{ (ads)} \qquad (1)$$

$$Ga(CH_3)_2 \text{ (ads)} \quad \text{-->} \quad Ga \text{ (ads)} + C_2H_6 \text{ (g)} \qquad (2)$$

$$2 Ga \text{ (ads)} \quad \text{-->} \quad Ga_2 \text{ (ads)} \qquad (3)$$
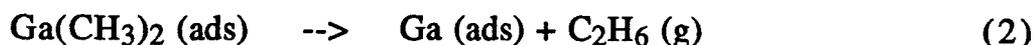
Reaction (2) proceeds to some extent at room temperature and goes essentially to completion by 150 °C.

This simple mechanism cannot be complete, since it cannot explain why some TMG fragments decompose completely to Ga and CH_3 groups immediately upon adsorption, while other decompose only partially to DMG fragments, which are then stable for long periods of time at 300 Kelvin. An understanding of the stability of the DMG fragments can be obtained by examining in more detail the adsorption process, particularly the role of surface defects. Figure 11 shows three STM images of a single region of the surface before exposure (11a) and after exposure (11b and 11c) to TMG. A comparison of these images shows that the DMG fragments are usually observed at locations where, prior to dosing, the surface contained a defect. Arrows in fig. 11 denote some of the locations where in (a) there are defects and in (b) and/or (c) there are DMG fragments bonded at the same location. A statistical analysis of such images shows that more than 85% of the observed DMG fragments (i.e., those that have not decomposed further) are bound at defects on Si(001). These fragments exhibit the greatest preference for binding at dimer vacancy defects, both single and double vacancies, and also show some preference for C-type defects. The role of the defect is thus to stabilize the intermediate DMG fragments; those

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which are bonded to defects are stable at 300 Kelvin, while those which are not bonded to defects tend to decompose quickly, on shorter time scales than we are able to image.

Our experiments show that the DMG fragments are somewhat mobile on the surface at room temperature. Comparison of figures 11b and 11c show that, after a 6 minute delay, some of the DMG's on the surface have disappeared from their original binding sites. The locations of the "missing" DMG's are labeled with "M" in figure 11c. Figure 13 shows more direct evidence for the mobility of DMG groups on the surface. This image shows four different types of mobile behavior by DMG groups, as indicated. Position 1 shows a DMG that changes its position, moving down its dimer row by one dimer, between two of the linescans of the STM. This is evidenced by the discontinuity of its appearance at one vertical position in the image. Position 2 shows a DMG which appears to be continuously flipping between two (or more) binding sites, giving it a smeared out, discontinuous appearance. Position 3 shows a DMG which disappears entirely between two linescans, while the DMG at position 4 appears suddenly at this binding site between two linescans, remains there for a short while, then disappears.

The fact that DMG fragments are mobile on the surface, rather than binding immediately at their reaction site, suggests a mechanism wherein the DMG fragments can move around on the surface for some period of time after their formation, before they decompose further to ethane and gallium. If in this time they find a stable binding site like a defect, they will tend to stick as dimethylgallium rather than decomposing further (at room temperature).

III. Comparison to Previous Work

It is useful to compare our results to previous experimental work on this system. R. I. Masel and coworkers [3, 5-7] used TPD, EELS, XPS and AES to investigate the decomposition of TMG on Si(001). Their results indicated that one atom of carbon is deposited on the surface for every atom of gallium, in agreement with our proposed mechanism. However, this group saw methane as a major TPD product and proposed a mechanism in which TMG decomposes intramolecularly in two steps. In each step, one CH_3 abstracts a hydrogen atom from another methyl group on the same TMG and leaves as CH_4. After the loss of two methane molecules, the carbon atom in the remaining CH group then bonds to the surface. Thus, Si-C bonds do not form until late in the decomposition process. This is

clearly not consistent with our results, which show C-Ga bond cleavage and Si-C bond formation as the first step in TMG decomposition. Flores et al. saw $SiCH_3+$ ions in SSIMS experiments on TMG-dosed Si(001) surfaces, even at a temperature of 115 K. These researchers also concluded that methyl group deposition onto the Si surface is an early step in TMG decomposition.

It is clear that, with diffusion of DMG fragments occurring at room temperature and with the possibility of both intermolecular and intramolecular elimination reactions, the chemistry of TMG on Si(001) will likely be dependent on coverage. Thus, at the higher coverages studied by Masel, et al., (≥ one monolayer), the TMG molecules may be close enough to each other on the surface to react *intermolecularly*, with methyl groups of one TMG molecule abstracting H atoms from the CH_3's of neighboring molecules, to leave as CH_4. At the lower, submonolayer coverages of our experiments, this reaction would not occur to any significant extent because, on average, the TMG molecules are too far apart. Instead, TMG's would land on the surface, lose a methyl group to the surface (on a timescale fast compared to STM imaging) and become DMG's. This coverage-dependent mechanism would explain the two apparently contradicting sets of results.

Conclusions

We have identified the molecular fragments in the adsorption and dissociation of trimethylgallium on Si(001). The primary fragments are CH_3, $Ga(CH_3)_2$, and gallium. Gallium atoms combine on the surface into dimers and tend to arrange themselves epitaxially in dimer rows running perpendicular to the underlying Si(001) dimer rows, as was observed by Nogami et al. [12-14]. Dimethylgallium fragments are slightly mobile on the surface and are preferentially stabilized when bonded at defect sites. We propose that adsorption and decomposition of submonolayer coverages of TMG on Si(001) at 300 K involves first a decomposition to a surface-bound methyl group and a dimethylgallium fragment. At room temperature the DMG fragment moves around the surface for a short time, during which it either finds a stable binding site or decomposes further. DMG decomposes to give a surface bound gallium atom and an ethane molecule, which escapes into the gas phase. DMG decomposition occurs to some extent at room temperature and goes essentially to completion by 150 °C. The gallium atoms so released combine to form rows of gallium dimers on the surface.

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Table I. Apparent Height of TMG Fragments in Filled/Unfilled
State Images (Height above Si(001) Dimers, Å). Heights
are believed accurate to ± 15%

Sample Bias:	Species:		
	CH_3	DMG	Ga_2
-2.4 V (filled states)	0.33	2.7	0.30
+2.7 V (empty states)	not measured	1.4	2.4

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Figure   Captions

Figure   1.
Large-scale STM image of a Si(001) surface dosed with
approximately 0.2 Langmuir of TMG.   Imaging conditions: Sample
Bias = -2.4 V , Tunneling Current = 0.3 nA, 265 Å x 300 Å.

Figure   2.
Small-scale, high-resolution STM image of a Si(001) surface dosed
with 0.2 L of TMG, showing "CH3", "DMG", and "Ga" features. Imaging
conditions: -2.4V, 0.3 nA, 115 Å x 90 Å

Figure   3.
Small-scale, high-resolution STM image of a Si(001) surface dosed
with 0.2 L of TMG then heated to 150 °C, showing "CH3" and "Ga"
features.   Imaging conditions: -2.4V, 0.3 nA, 95 Å x 95Å.

Figure   4.
STM image of Si(001) dosed with 0.2 L of TMG and heated to 150 °C.
Several "Ga2" building-block features are labeled.

Figure   5.
STM image of a single region of a Si(001) surface dosed with 0.2 L of
TMG, imaged using a sample bias of (a): -2.4 V (filled states), (b) +2.7
V (empty states, identical area).   Both (a) and (b) show "DMG" and
"Ga" features.

Figure   6.
Diagram showing the appearance and symmetry of the various TMG
fragments at (a) negative sample bias, and (b) positive sample bias.

Figure   7.
Two models for Ga$_2$ bonding on Si(001): (a) the parallel dimer model;
(b) the perpendicular dimer model.

Figure   8.
Small area, high-resolution STM image of several "CH3" features,
which are marked with arrows.   The horizontal gridlines mark the
centers of the Si(001) dimer rows in this image.   Imaging conditions:
-2.4V, 0.3 nA, 25 Å X 25 Å.

Figure   9.
Bonding configuration for a CH$_3$ group on Si(001).

Figure 10.
(a) High-resolution STM image of several DMG features. Gridlines mark the spaces between neighboring silicon dimers of the Si(001)(2x1) reconstruction, and show the symmetry of the DMG features with respect to the underlying Si lattice. Imaging conditions: -1.8 V, 0.3 nA, 45 Å x 32 Å.
(b) Diagram of the binding geometry of a DMG fragment on the Si(001) surface.

Figure 11.
Series of STM images of an identical area of a Si(001) surface at various stages of TMG exposure. This surface was exposed to a low pressure (approximately 5 x 10^{-10} T) of TMG for (a) zero minutes, (b) 4 min., (c) 10 min. The notations in the various images are explained in the text. Imaging conditions: -2.4 V, 0.3 nA, 140 Å x 170 Å.

Figure 12.
STM images of a Si(001) surface dosed with 0.2L of TMG (a) before, and (b) after heating to 150 °C for 2 minutes. Imaging conditions: -2.0 V, 0.3 nA, 190 Å x 190 Å.

Figure 13.
STM image of a TMG-dosed Si(001) surface showing mobility of DMG groups on the surface. Features 1 - 4 are described in the text.

DMG

Ga
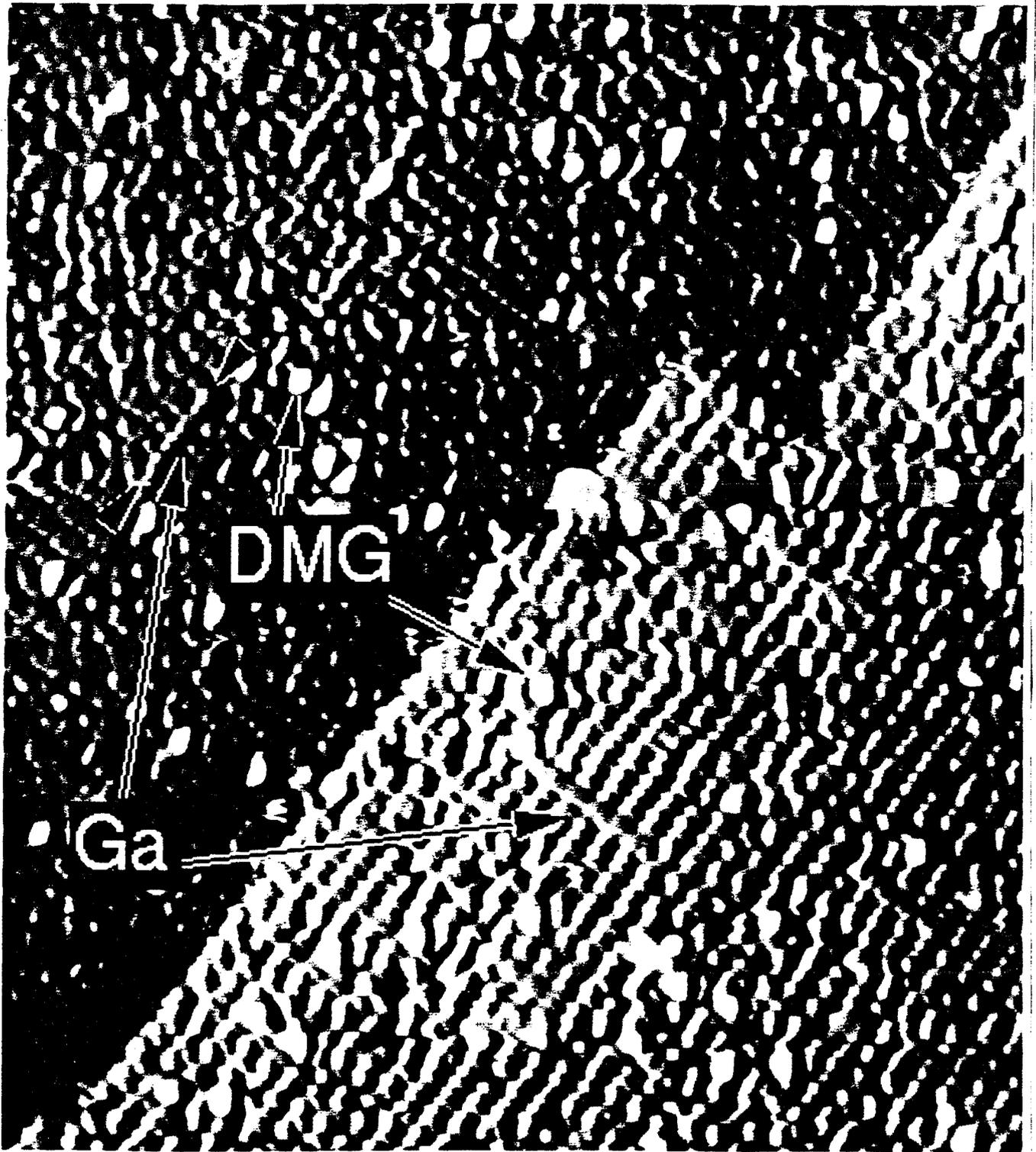
Bronikowski and Hame
Figure 1

Ga

CH3
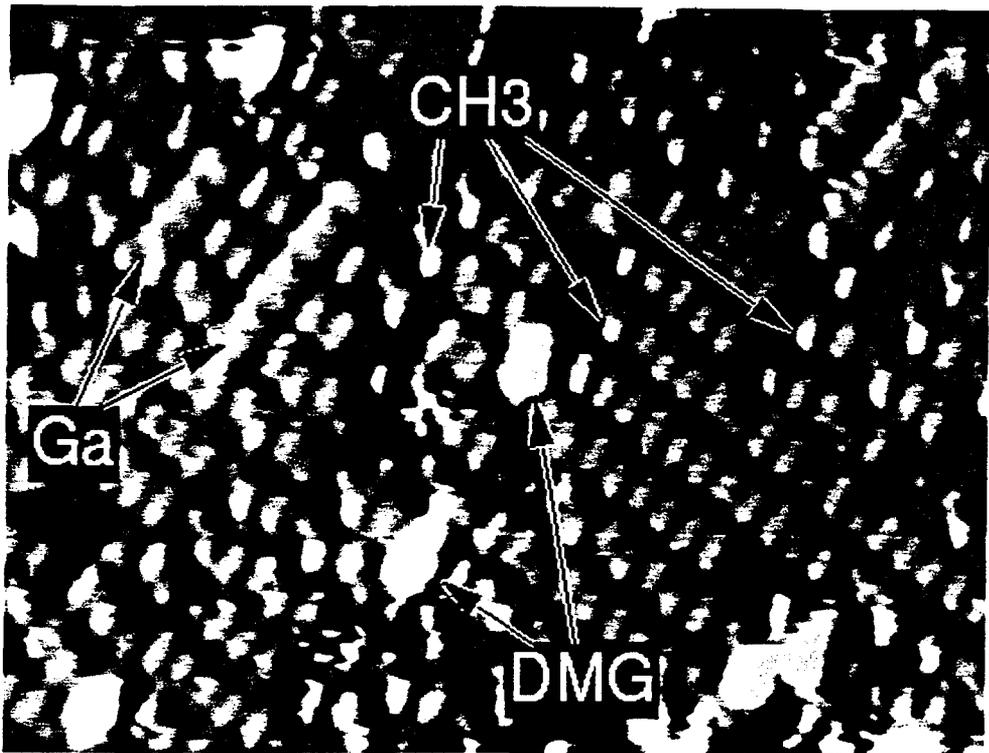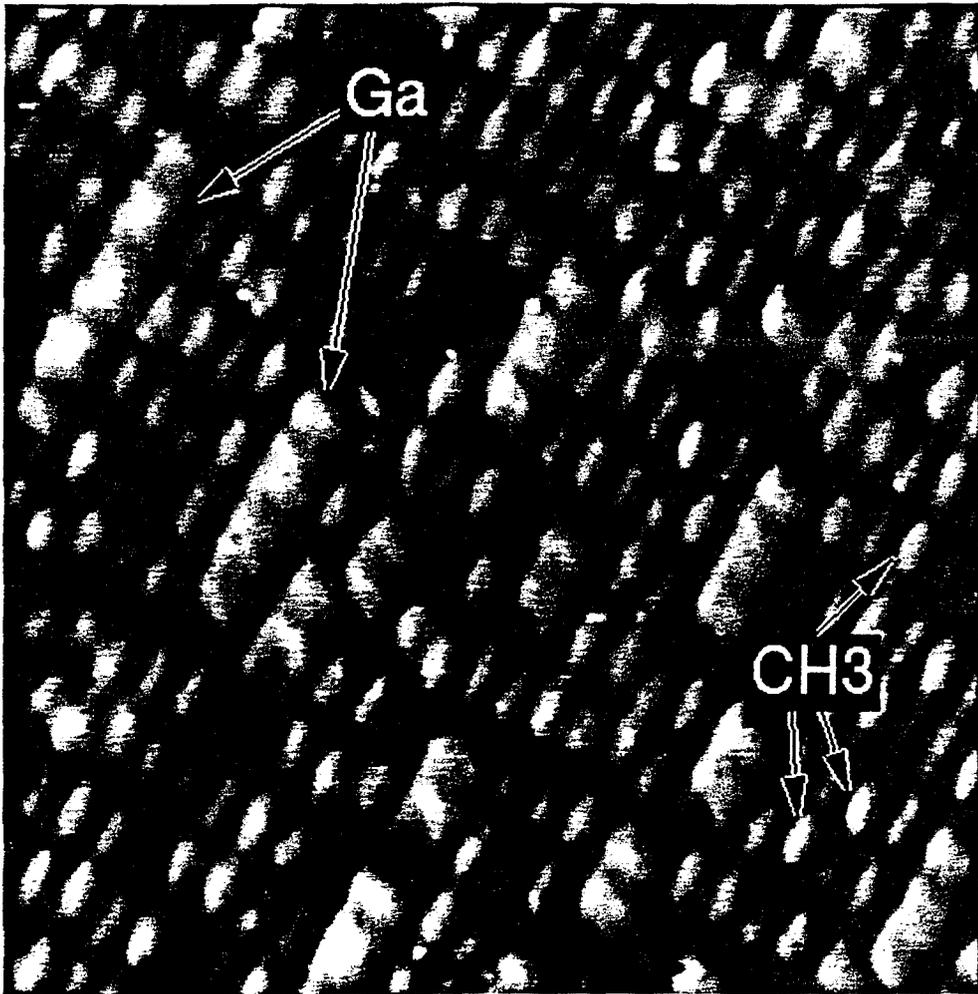
Bronikowski and Hamer
Figure 3

Ga2
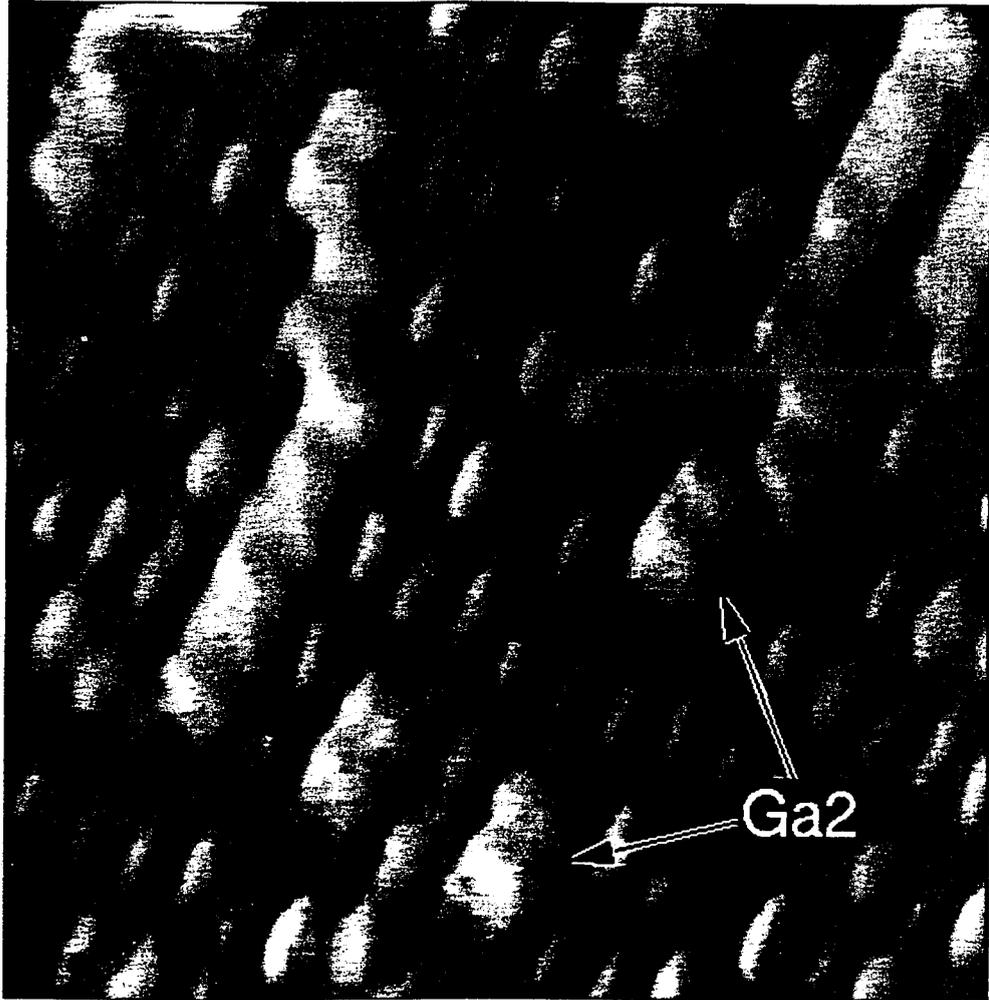
Bronikowski and Hame
Figure 4
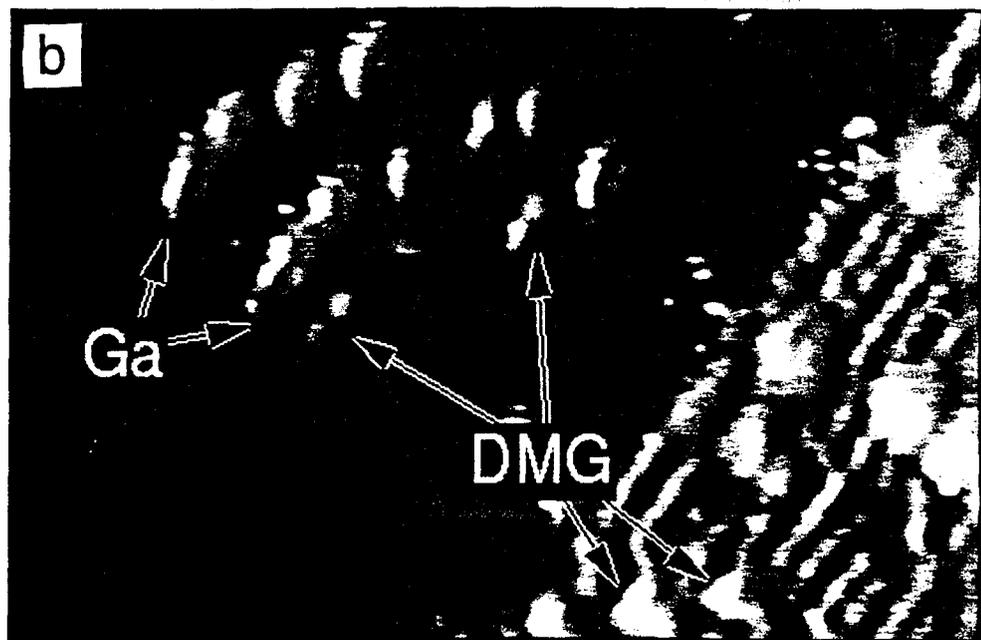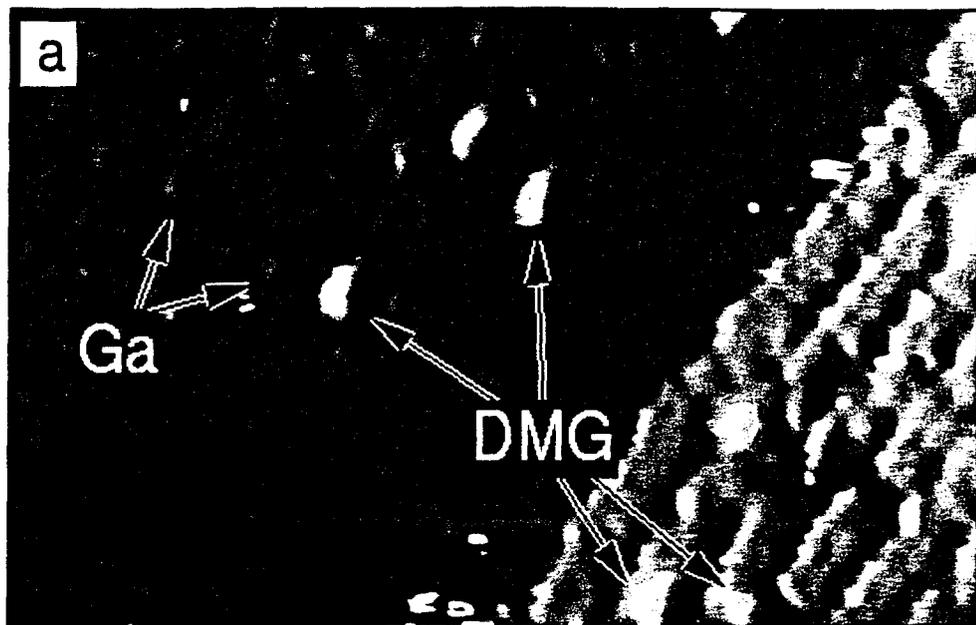
a) Filled State (Negative Bias)

DMG

Ga Dimer String

Ga2

CH₃
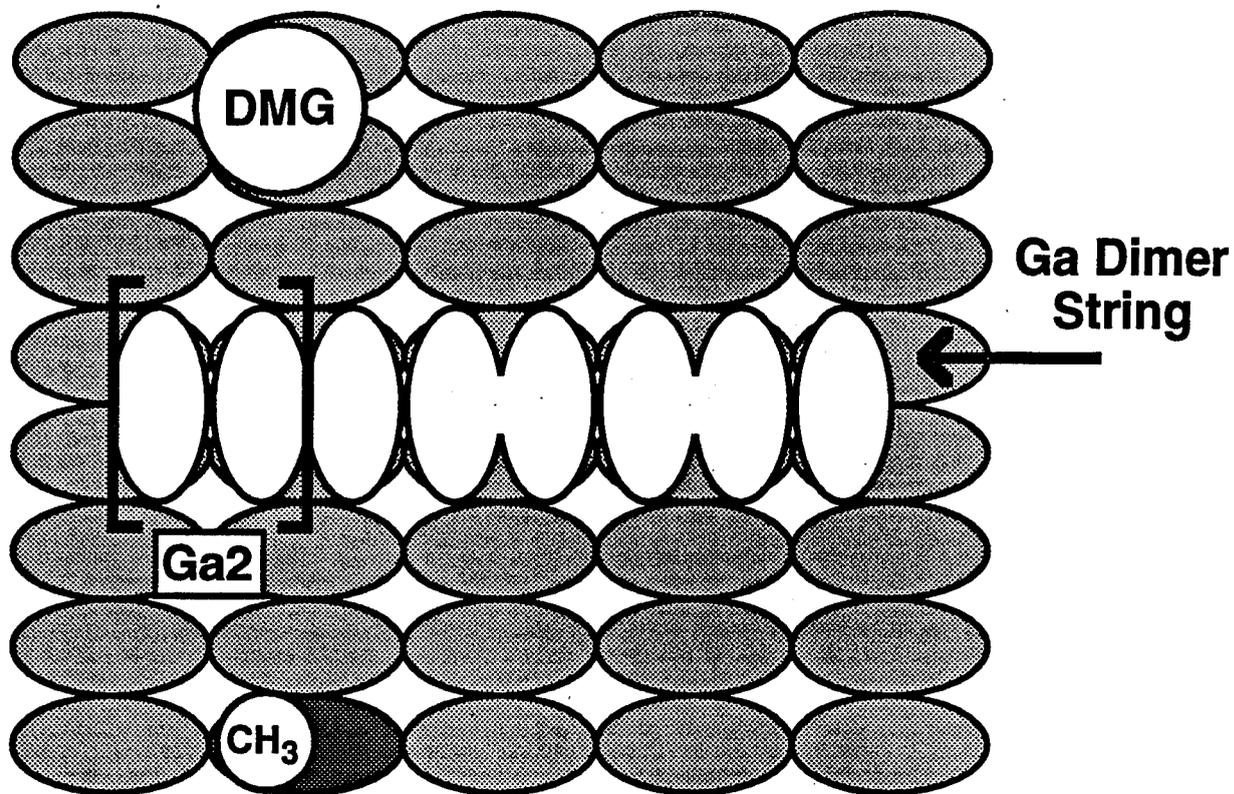
# b) Empty State (Positive Bias)

DMG

Ga Dimer String

Ga2

CH₃
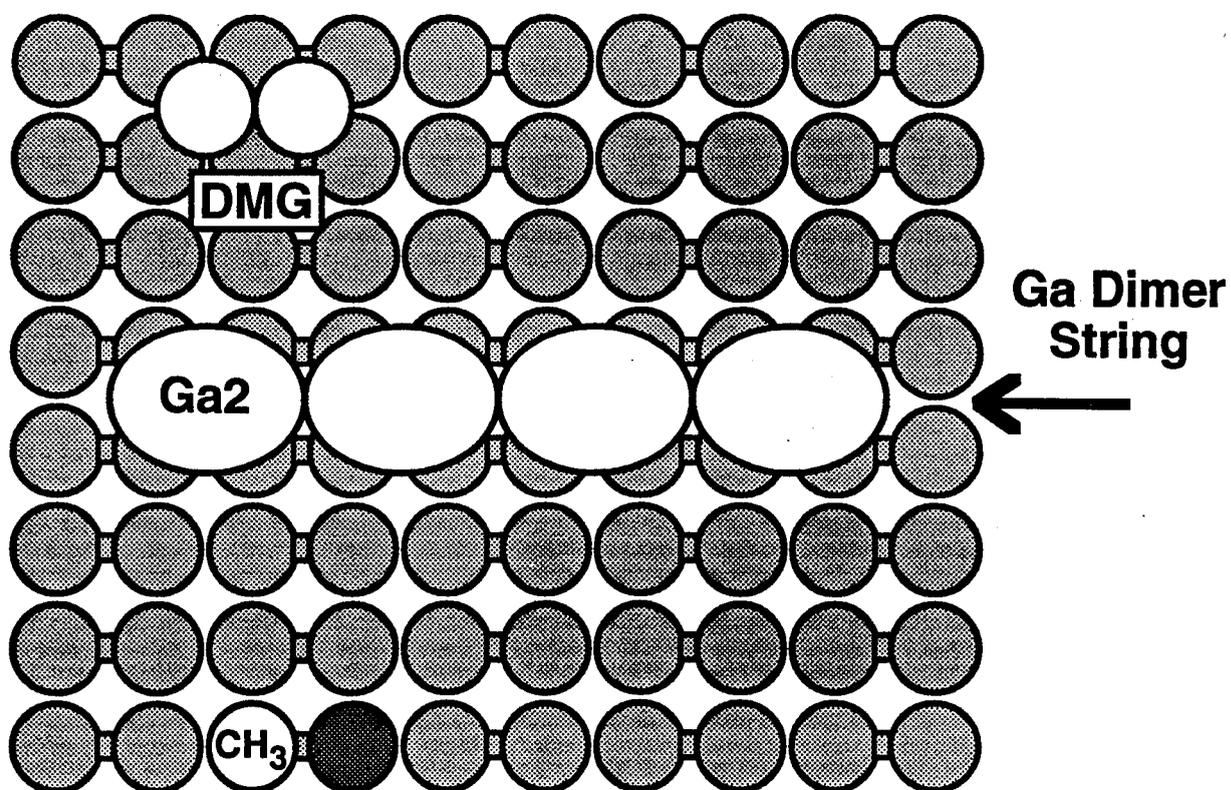
a) Parallel Dimer Model

b) Perpendicular Dimer Model

a

b
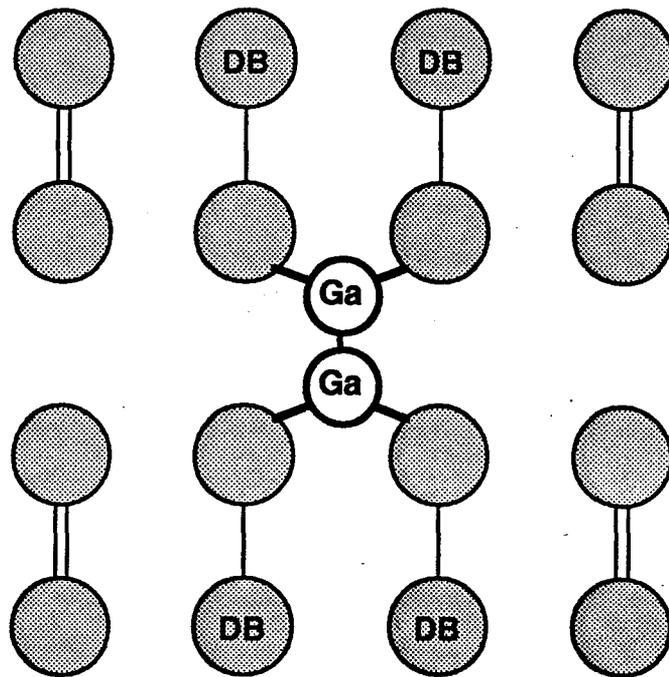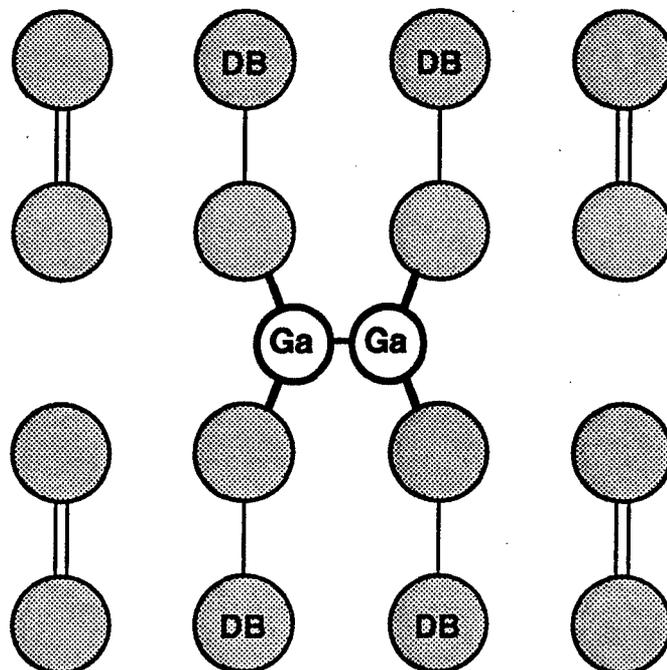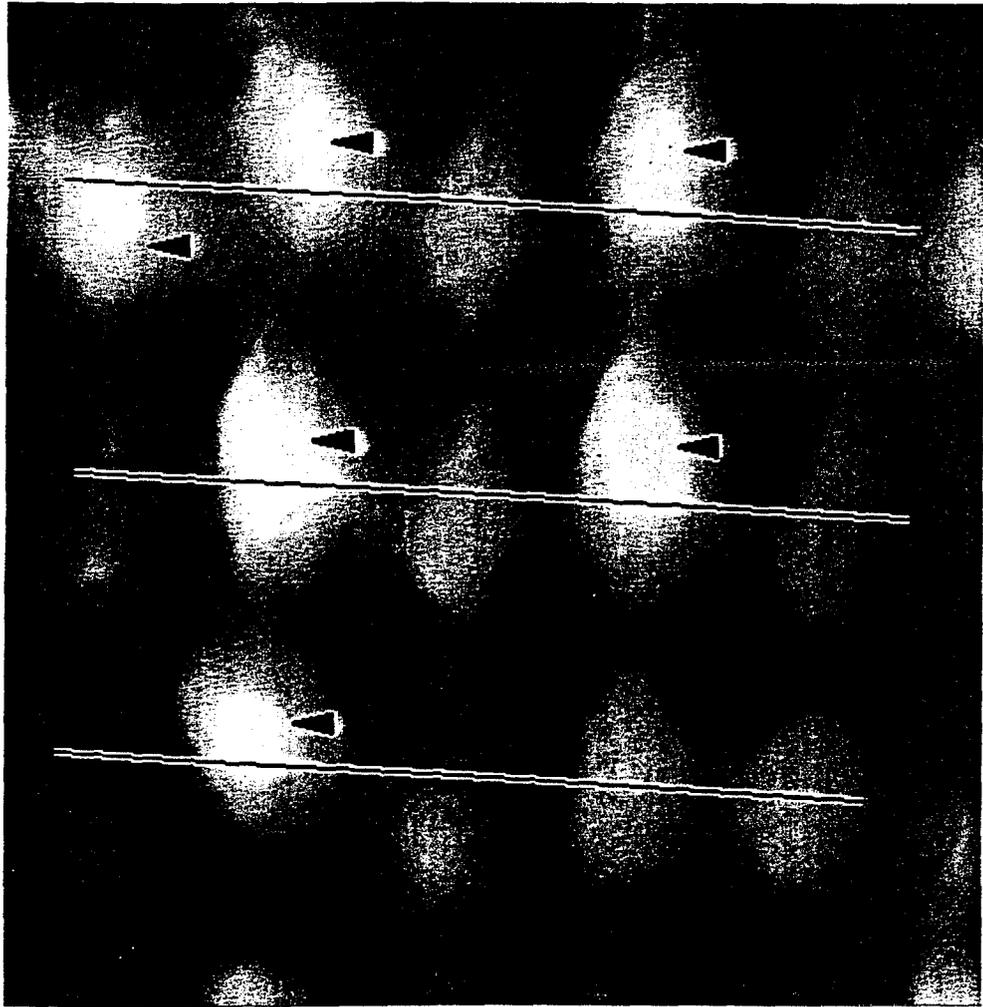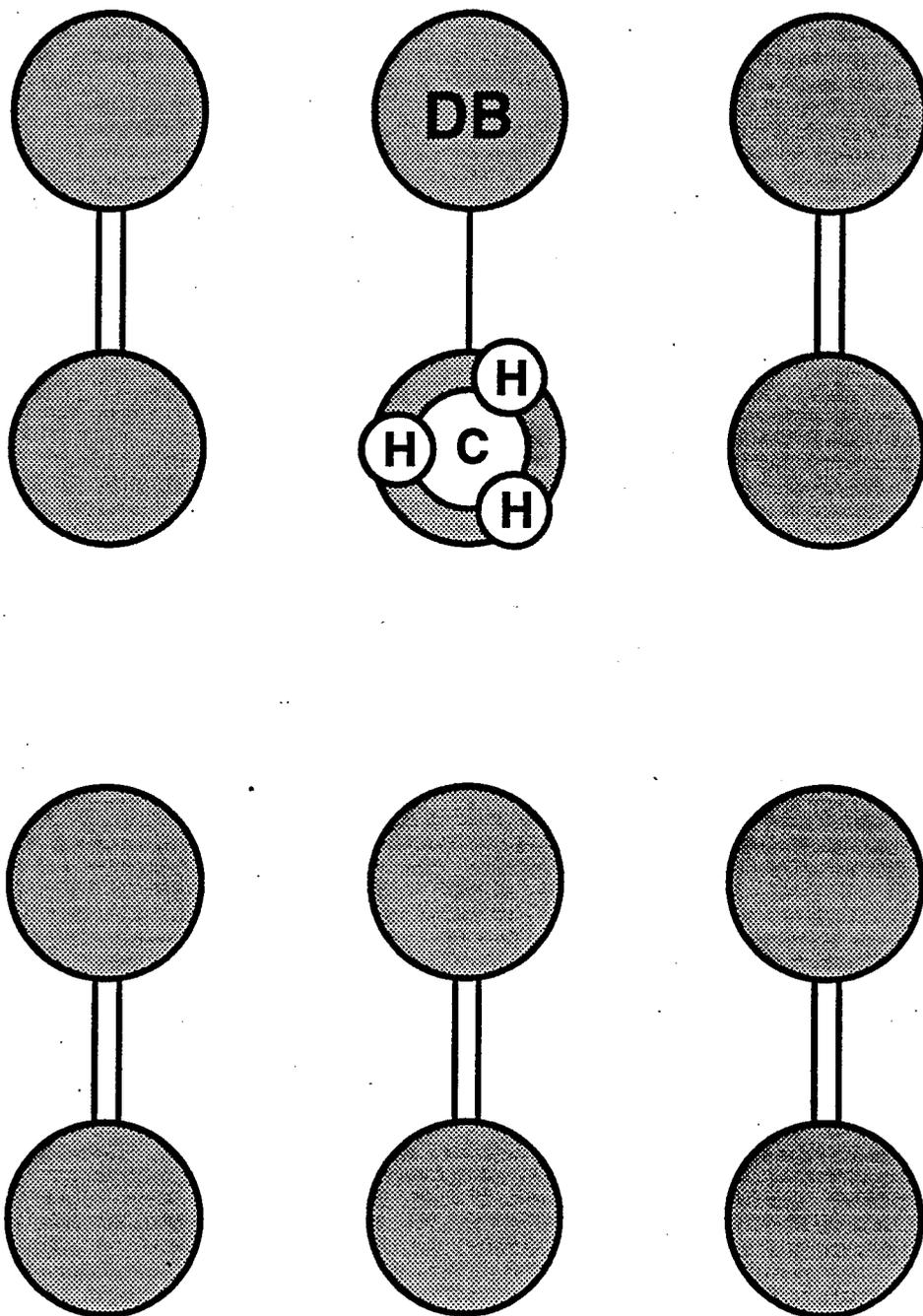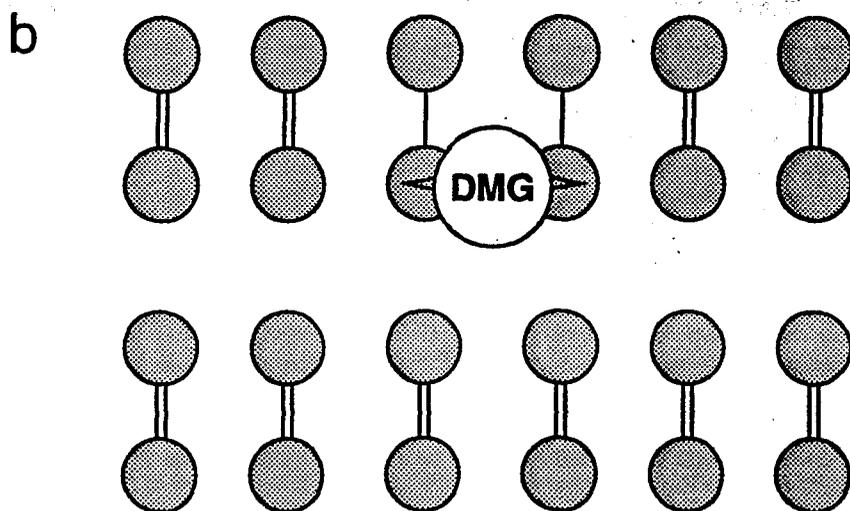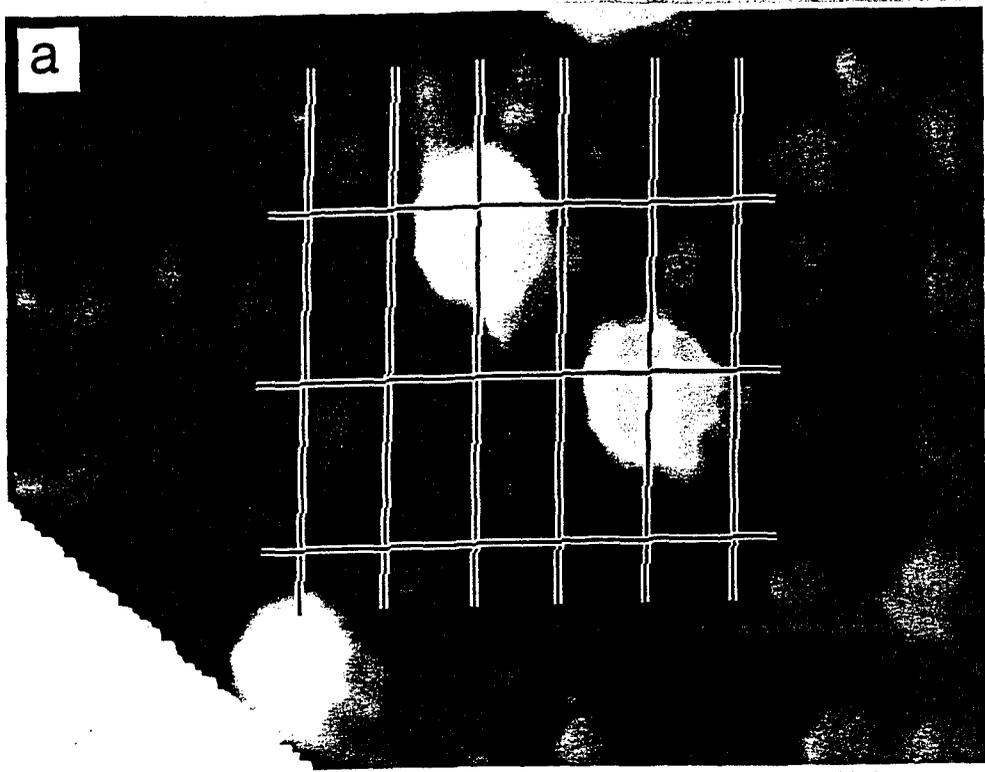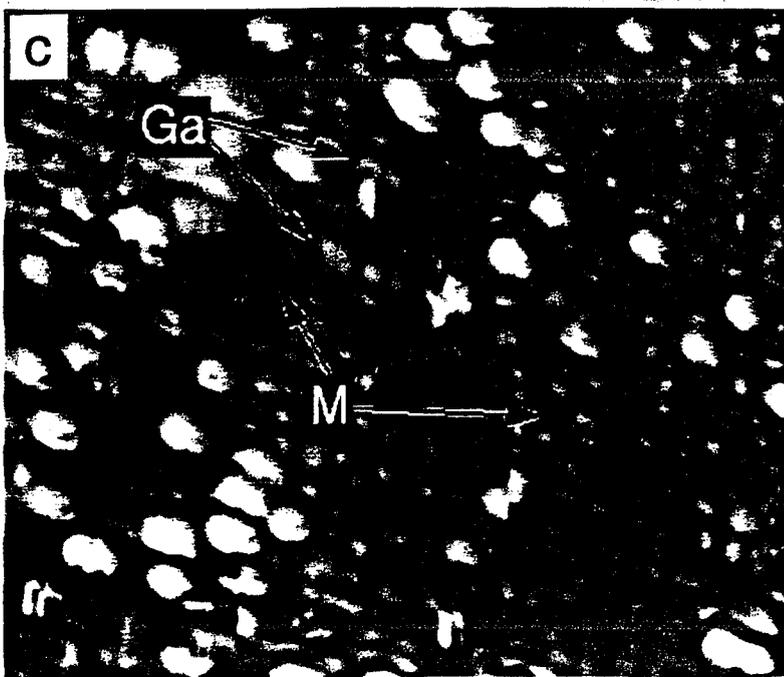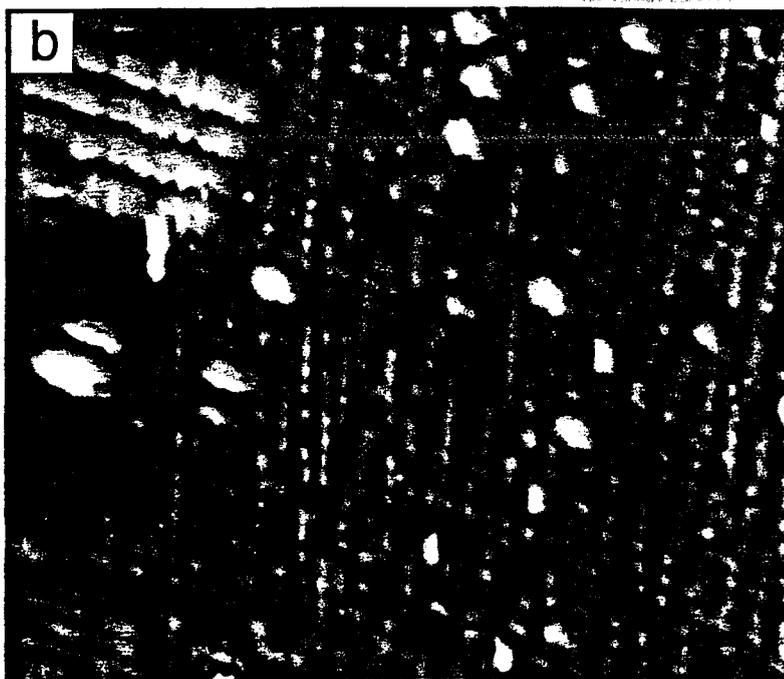
Bronikowski and Hamers
Figure 13